Tricritical points in bimodal polymer solutions

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Tricritical points in bimodal polymer solutions

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The tricritical point of polymer solutions composed by two polymer homologs of different molecular weight in a solvent is studied using the single-chain mean-field theory. The tricritical point is found for a ratio of molecular weights of the two polymers $r=N_1/N_2$, which decreases as a function of the short chain length N_2 from 51 to approximately 40 for N_2 increasing from 1 to 8. This last value is still much larger than the experimentally measured value for mixtures of polystyrene in cyclohexane, where it was found that $r\simeq 25$. Although a further reduction of r as a function of N_2 seems likely, the chain lengths of the corresponding long chains are beyond the reliability limit of the SAW's simulation involved. The addition of a small effective repulsion between the polymer homologs, is found to bring down the predicted value to 25. © *1996 American Institute of Physics.* [S0021-9606(96)50416-7]

I. INTRODUCTION

The possibility of having three phases in equilibrium for a solution of two polymer homologs of high molecular weight was already pointed out by Tompa,[1] who estimated that this can only be achieved if the ratio between the two molecular weights, r, is of the order of 10 or higher. Later Solc[2,3] realized that this lower bound corresponds to a tricritical point, i.e., for this particular ratio $r_t\simeq 10$, the three phases in equilibrium become identical. At fixed pressure, a tricritical point can only be observed in a ternary mixture if some other variable can be varied systematically. In solutions of two different chain molecules that are chemically identical but differ in degree of polymerization, the fourth parameter, besides temperature and two concentrations, is most conveniently found in the chain length of the shortest chain. The three-phase equilibrium is usually discussed in terms of the ratio r for reasons that will become clear. Three-phase equilibrium has been observed for a few bimodal polymer solutions, notably polyethylene–diphenylether,[4] polystyrene–cyclohexane,[5,6] and polystyrene–methylcyclohexane.[7] Sundar and Widom[8] investigated bimodal polystyrene solutions in cyclohexane in order to locate the tricritical point. Different values of r were obtained by selecting different pairs of molecular weights from a series of molecular weights consisting of $M_w=35\times10^3$, 48×10^3, 68×10^3 g mol^{-1} for the low molecular weight component and $M_w=0.93\times10^6$ and 1.8×10^6 g mol^{-1} for the high molecular weight components. All polymers involved were polystyrene standards of a dispersity smaller than 1.1. On the basis of their results, the authors concluded that $r_t\simeq 25$, much higher than the value estimated by Tompa. Most recently, Shen *et al.*[9] studied slightly different molecular weights of bimodal polystyrene in methylcyclohexane and found $r_t\simeq 23$ in very good agreement with Sundar and Widom measurements.

In a subsequent theoretical analysis by Broseta,[10] the tricritical point in bimodal polymer solutions was considered once more in the framework of the Flory–Huggins theory, however this time starting from its virial expression,

$$F/kT=\frac{\phi_1}{N_1}\ln\phi_1+\frac{\phi_2}{N_2}\ln\phi_2+\frac{1}{2}v\phi^2+\frac{1}{6}w\phi^3+\cdots, \tag{1}$$

where ϕ_1 and ϕ_2 are the volume fraction of the polymer molecules with length N_1, respectively, N_2, $\phi=\phi_1+\phi_2$ is the total volume fraction of polymer and v and w represent the second and third virial coefficients. The last two terms arise from the virial expansion of the original Flory–Huggins expression, i.e., from

$$(1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)\simeq\left(\frac{1}{2}-\chi\right)\phi^2+\frac{1}{3}\phi^3+\cdots, \tag{2}$$

where terms linear in ϕ have been dropped. Using the virial expansion, stopped after the third order, an analytic expression for the critical volume fraction and the critical value of the second virial coefficient (i.e., critical temperature) was obtained, which resemble closely the exact expressions derived long ago by Koningsveld.[11] From an analysis of the critical temperature as function of the fraction x of monomers belonging to the long chain ($x=\phi_2/\phi$) an algebraic equation for the value of $r=N_1/N_2$ at the tricritical point was obtained. From this equation it followed easily that

$$r_t=5+2\sqrt{6}\simeq 9.899. \tag{3}$$

The above analysis is only valid in the long chain limit. In Ref. 2, Solc demonstrated that as a function of the short chain length N_2, r_t decreases monotonously from approximately 16 to this limiting value. So, the Flory–Huggins theory clearly predicts a much smaller value than observed. In closely related experiments Scott, Knobler, and co-workers[12–14] studied mixtures of ethane and n-alkanes locating the fluid–fluid–vapor tricritical point somewhere in

between $n=17$ and 18. In this case the role of the solvent is taken by the empty ''sites'' and their results imply a value of $r_t \simeq 9$. Here, the pressure plays the role of the fourth variable, and these systems can not be compared directly with bimodal polymer solutions at constant pressure. On the other hand they do form a strong indication for the nonuniversality of r_t.

Confronted with the large discrepancy between the theoretically predicted $r_t \simeq 10$ and the experimentally (PS/cyclohexane) observed value of $r_t \simeq 25$, we decided to apply a theoretical model developed some years ago by one of us to this problem.[15] Compared to the Flory–Huggins theory, the essential improvement consists in the fact that the intramolecular interactions and conformational entropy of each molecule are taken into account rather accurately and even exact in the infinite dilution limit. Realizing the low concentrations involved in phase separated polymer solutions, its importance is easily appreciated. This theoretical approach was originally developed to treat surfactant molecules in amphiphilic aggregates[16] and later generalized to bulk[15] and inhomogeneous polymeric systems.[17] In a recent paper we discussed its application to polydisperse systems and demonstrated that it correctly predicted the behavior of the distribution coefficient as function of the chain length.[18] Here, the Flory–Huggins theory predicts a linear relationship, whereas in reality the dependence is considerably weaker. Furthermore, it is the first theoretical approach that predicts correctly the chain length dependence of the critical volume fraction in binary polymer solutions.[15] It seems therefore ideally suited to study tricritical phenomena in bimodal polymer solutions.

II. THEORETICAL APPROACH

Consider a mixture of two polymers composed of the same monomers, n_1 polymer molecules of N_1 monomers and n_2 polymers of N_2 monomers, together with a solvent in a lattice of M sites. All lattice sites are occupied by solvent molecules or monomers. Although, the following steps are well known, they are repeated here to facilitate a slight adaptation that will be introduced further on. The Helmholtz free energy of this system can be written as

$$F/kT=\sum_{i=1,2}\left[n_i \ln \phi_i + n_i \sum_{\{\alpha\}} P_i(\alpha) \ln P_i(\alpha) + \chi n_i \langle n_{N_i}\rangle \phi_s\right] + n_s \ln \phi_s, \tag{4}$$

where the first and last term represent the translational entropy of the chain molecules and solvent molecules. The number of solvent molecules is n_s and their volume fraction ϕ_s. Since all lattice sites are occupied, $M=n_1N_1+n_2N_2+n_s$. The second term represents the conformational entropy of the chain molecules expressed in terms of the probability distribution function (pdf) of chain conformations, $P_i(\alpha)$. The set of conformations $\{\alpha\}$ obviously differs for the two different polymer species involved. Averages like the average number of intermolecular contacts of polymer i, $\langle n_{N_i}\rangle$ are calculated with respect to the pdf. The third term therefore represents the number of intermolecular contacts multiplied by the mean-field probability that the contact is with the solvent. χ represents as usual the exchange interaction parameter in units kT, i.e., $\chi=[\epsilon_{ps}-(\epsilon_{pp}+\epsilon_{ss})/2]/kT$. It differs from the Flory–Huggins parameter by the absence of the lattice coordination number. Minimizing the free energy, Eq. (4), with respect to the pdf gives straightforwardly,

$$P_i(\alpha)=\frac{1}{q_i}\exp[-\chi n_{N_i}(\alpha)\phi_s], \tag{5}$$

where q_i is the single chain partition function ensuring proper normalization of the pdf. This expression demonstrates the unique feature of this approach, the coupling between the chain conformations, and the thermodynamic state. Through the solvent volume fraction and the interaction parameter, the pdf depends on composition as well as temperature. Substituting Eq. (5) into Eq. (4) leads to the following expression for the free energy:

$$F/kT=\sum_{i=1,2}[n_i \ln \phi_i - n_i \ln q_i] + n_s \ln \phi_s. \tag{6}$$

The essential new element in this expression is the single chain partition function q_i. Assuming the number of intermolecular contacts to be independent of the conformation Eq. (6) immediately leads back to the familiar Flory–Huggins expression. In order to apply this to various problems q_i is calculated by generating a fixed representative set of self-avoiding walks of a specified length on a cubic lattice. This procedure has been described in great detail in the literature.[15] Then the critical points are calculated from the spinodal equation

$$Z=\frac{\partial^2 F}{\partial \phi_1^2}\frac{\partial^2 F}{\partial \phi_2^2}-\left[\frac{\partial^2 F}{\partial \phi_1 \partial \phi_2}\right]^2=0 \tag{7}$$

and

$$\det\begin{bmatrix} \dfrac{\partial Z}{\partial \phi_1} & \dfrac{\partial^2 F}{\partial \phi_1 \partial \phi_2} \\ \dfrac{\partial Z}{\partial \phi_2} & \dfrac{\partial^2 F}{\partial \phi_2^2} \end{bmatrix}=0. \tag{8}$$

III. RESULTS AND DISCUSSION

Both equations have been solved numerically using Eq. (6) for various different pairs of chain lengths. Figure 1 presents a picture of the critical temperature as a function of $x=\phi_2/(\phi_1+\phi_2)$ for a pair of chain lengths 322, 8 ($r=40.25$). In this case the critical temperature is a monotonic function of x so that there is at most one critical point for a given temperature. Figure 2 on the other hand represents the situation for a pair of chain lengths 336, 8 ($r=44$). Now the critical temperature is a nonmonotoneous function of x and a stability analysis shows that the portion in between the two extrema is unstable. In that region a separation in three phases occurs. In this way, the tricritical temperature could

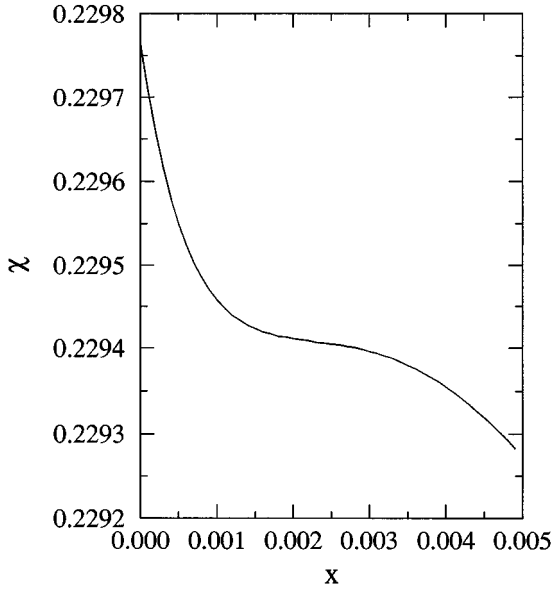

FIG. 1. Critical interaction parameter as a function of the composition of a long polymer for a mixture with $N_{short}=8$, $N_{long}=322$. Note that the critical interaction parameter is a monotic function of the composition.

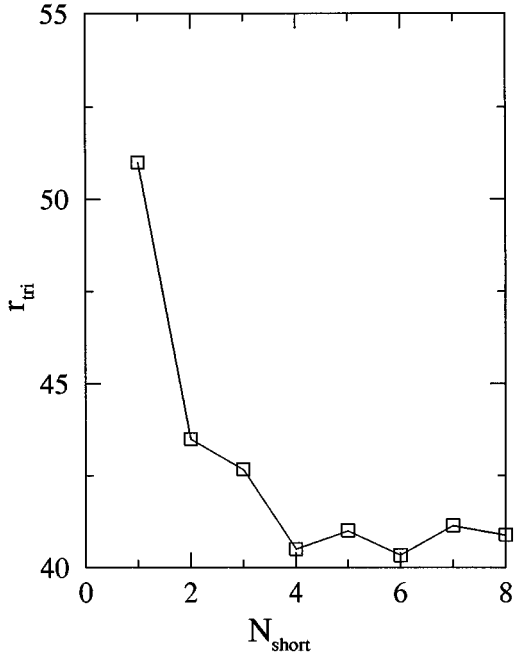

FIG. 3. Critical value r_t as a function of N_{short}.

be located at $r_t \simeq 41$ for $N_2=8$. For the range of chain lengths investigated, 1–8 for the short chains and 40–336 for the long chains this tricritical value is found to decrease first but then to level off. Figure 3 demonstrates this behavior with a characteristic odd–even effect superimposed on it. Since, in the Flory–Huggins theory, r_t is a monotonic decreasing function of N_2, which continues to decrease with more than 20% beyond $N_2=8$, it is not unreasonable to expect a similar behavior for our approach. In both cases, the decrease is obviously due to the combinatorial entropy which is the same in both models. We tentatively attribute the strong leveling off around $N_2=6$–8 observed to less accurate sampling of the very long SAW's involved, i.e., $N_1>300$. Nevertheless, a considerable difference with the experimental value $r_t \simeq 25$ observed for PS/cyclohexane (or methylcyclohexane) (Refs. 8,7,19) seems to remain.

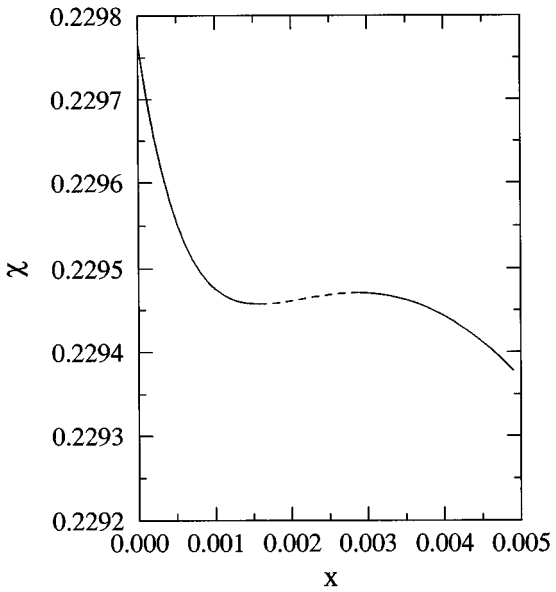

FIG. 2. Same as Fig. 1 but for $N_{short}=8$, $N_{long}=336$. Note in this case the nonmonotic behavior of the critical interaction parameter. The dashed line represents the regime for which the critical system is not stable.

If real, this deviation must be related to the fact that our free energy expression does not accurately describe these kind of ternary solutions. Deviations from predictions made by the Flory–Huggins theory for dilute and semidilute solutions come as no surprise. However, it is precisely in this regime that our approach has been demonstrated to present a considerable improvement. One possible explanation for the discrepancy between our result and the experimental observation could be the fact that chemically identical polymers of vastly different chain lengths do not interact athermally which each other, or interact differently with the solvent. Arguments to support this come from known compressibility effects (polyethylene in *n*-alkanes show lower critical solution temperature behavior[20]) but also from the much debated polyethylene blends of different PE-grade. Besides these possibilities, we also realize that our model treats the intermolecular correlations in the mean-field approximation. This might have important consequences as the following analysis demonstrates. In temperature, the tricritical point occurs close to the critical temperature of the short chain solvent system and the following qualitatively correct picture emerges from the Flory–Huggins description. On the basis of Broseta's result[10] and well known results for binary polymer solutions it follows that

$$\theta - T_{c1} : \theta - T_t : \theta - T_{c2} \simeq 1 : 0.989 : 0.316, \tag{9}$$

where T_{ci} is the critical temperature of the pure polymer i/solvent system. The value of 0.989 is derived by Broseta, whereas the value of 0.316 equals $1/\sqrt{N_2/N_1} = 1/\sqrt{r}$. Furthermore, the fraction of monomers belonging to the long chains at the tricritical point was shown to be $x_t \simeq 0.0101$, which is extremely small. Finally, the tricritical total monomer volume fraction at the tricritical point ϕ_t compared to the monomer volume fraction ϕ_{1c} at the critical point of the pure short chain solution is given by $\phi_t/\phi_{1c} \simeq 1.237$. Experimentally, extremely close to tricritical conditions Sundar and Widom[8] observed for PS ($M_w = 68\,000$) and PS ($M_w = 1.8 \times 10^6$) in cyclohexane a three phase interval over $\Delta T \simeq 0.02$ °C, however, the composition of the long chains was still very asymmetric with hardly any long chains in the most diluted phase. The short chains on the other hand were far more evenly distributed. From de Gennes work[21] it is well known that the θ-region in the temperature-composition plane of a pure polymer solvent mixture just includes the critical point. The result presented in the last equation therefore implies that at the tricritical point, which is in between the two critical points but much closer to the short chain critical point, the short chains are in a θ-state, whereas the long chains are already entering the collapse regime. Of course, they are not fully collapsed and the ensemble of SAW's generated to discuss its phase behavior with our theory are still fully satisfactory[22] for not too high chain lengths. Therefore, the influence of the solvent quality on the average polymer conformation is believed to be handled already quite well by our approach. However, as mentioned before, the intermolecular correlations are only treated in the mean-field approximation. A striking effect of intermolecular correlations is seen in the opposite case of a ternary solution of two different ''incompatible'' polymers $P(A)$ and $P(B)$ in an equally good solvent for both, a reduction of the mean-field χ_{AB} occurs due to excluded-volume effects ($A-B$ contacts are avoided over the length scale of the ''blob size'' describing the screening of excluded-volume interactions).[23,24]

To estimate the order of magnitude that is required to obtain a value of r_t close to 25 already for the small values of N_2 involved, we decided to introduce an effective unfavorable interaction χ_{12} between the short and long chains. This is also of interest from a different point of view, since the most obvious extension of the Widom experiments is obtained by taking one of the components deuterated. This would, among others, introduce a small unfavorable interaction between both polymer homologs. Instead of Eq. (1) we now have

$$F/kT = \sum_{i=1,2} \Bigg[n_i \ln \phi_i + n_i \sum_{\{\alpha\}} P_i(\alpha) \ln P_i(\alpha) + \chi n_i \langle n_{N_i} \rangle \phi_s + \frac{\chi_{12}}{2} n_i \langle n_{N_i} \rangle \phi_j \Bigg] + n_s \ln \phi_s, \quad (10)$$

where $j = 2$ when $i = 1$ and reverse. Going through the same minimization procedure as before leads to a free energy expression

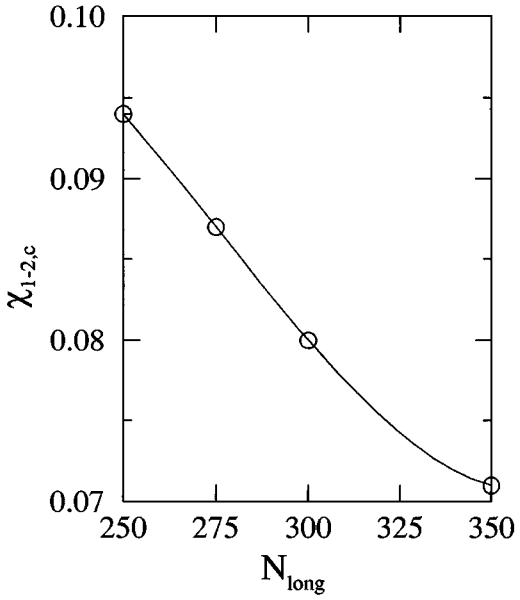

FIG. 4. The value of the effective polymer–polymer repulsion at the tricritical point as a function of the length of the long chain. All the results correspond to a fixed ratio of chain lengths, $r_t = 25$.

$$F/kT = \sum_{i=1,2} [n_i \ln \phi_i - n_i \ln q_i] + n_s \ln \phi_s \quad (11)$$

with

$$q_i = \sum_{\{\alpha\}} \exp\left[-\chi n_{N_i}(\alpha) \phi_s - \frac{\chi_{12}}{2} n_{N_i}(\alpha) \phi_j \right], \quad (12)$$

where j should be interpreted as before. Figure 4 presents the value of χ_{12} required to obtain $r_t = 25$ as a function of N_2. It demonstrates that the value needed to bring r_t down to 25 decreases rapidly for increasing values of N_2. It is a small fraction of the polymer–solvent interaction at the tricritical point. Hence, only an extremely small value seems to be required for the kind of molecular weights involved in the experimental studies.

IV. CONCLUDING REMARKS

Much to our surprise, the tricritical value of the ratio between the molecular weights of the two polymer homologs evaluated with the new solution theory, turned out to exceed 40, much higher than the experimental value of 25 for PS in cyclohexane and methyl cyclohexane, which in turn is much higher than the Flory–Huggins prediction of 10. Whereas the failure of the Flory–Huggins theory for these type of systems comes as no surprise, the large deviation from our predicted value is more difficult to understand. At least part of it we attribute to the small values of the chain length of the short chains involved. To what extent this can explain the large difference awaits further investigations involving longer ''short'' chain molecules. This requires a careful investigation of the possibilities to simulate representative samples of SAW's of lengths of 500 and higher. On the other hand, as demonstrated, already a small effective repulsion between

the two polymer homologs will bring the tricritical molecular weight ratio within the experimental range. Apparently, the location in terms of the molecular weight ratio is extremely sensitive to the precise thermodynamics. These observations also suggest that r_t is not necessarily a universal constant for high molecular weight bimodal polymer solutions and it would be very interesting to see experimental results for completely different systems. In the same spirit, experiments using two polymer homologs with one of the species deuterated are also of great interest.

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[1] H. Tompa, Trans. Faraday Soc. **45**, 1142 (1949).
[2] K. Solc, J. Polym. Sci. Polym. Phys. Ed. **20**, 1947 (1982).
[3] K. Solc, L. A. Kleintjens, and R. Koningsveld, Macromolecules **17**, 573 (1984).
[4] R. Koningsveld and A. J. Staverman, Kolloid Z. Z. Polym. **220**, 31 (1967).
[5] R. Koningsveld, L. A. Kleintjens, and A. R. Shultz, J. Polym. Sci. Part A2 **8**, 1261 (1970).
[6] Y. Einaga, Y. Nakamura, and H. Fujita, Macromolecules **20**, 1083 (1987).
[7] T. Dobashi and M. Nakata, J. Chem. Phys. **84**, 5775 (1986).
[8] G. Sundar and B. Widom, Fluid Phase Equilibria **40**, 289 (1988).
[9] W. Shen, G. R. Smith, C. M. Knobler, and R. L. Scott, J. Phys. Chem. **94**, 7943 (1990).
[10] D. Broseta, J. Chem. Phys. **91**, 1897 (1989).
[11] R. Koningsveld and A. J. Staverman, J. Polym. Sci. C **16**, 1775 (1967).
[12] J. Specovius, M. A. Leiva, R. L. Scott, and C. M. Knobler, J. Phys. Chem. **85**, 2313 (1981).
[13] M. C. Goh, J. Specovius, R. L. Scott, and C. M. Knobler, J. Chem. Phys. **86**, 4120 (1987).
[14] M. C. Goh, R. L. Scott, and C. M. Knobler, J. Chem. Phys. **89**, 2281 (1988).
[15] I. Szleifer, J. Chem. Phys. **92**, 6940 (1990).
[16] A. Ben-Shaul, I. Szleifer, and W. M. Gelbart, J. Chem. Phys. **83**, 3597 (1985).
[17] M. A. Carignano and I. Szleifer, J. Chem. Phys. **98**, 5006 (1993).
[18] G. ten Brinke and I. Szleifer, Macromolecules **28**, 5434 (1995).
[19] M. Nakata and T. Dobashi, J. Chem. Phys. **84**, 5782 (1986).
[20] R. A. Orwoll and P. J. Flory, J. Am. Chem. Soc. **89**, 681 (1967).
[21] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1985).
[22] I. Szleifer, E. M. O'Toole, and A. Z. Panagiotopoulos, J. Chem. Phys. **97**, 6802 (1992).
[23] J. F. Joanny, L. Leibler, and R. J. Ball, J. Chem. Phys. **81**, 4640 (1984).
[24] D. Broseta, L. Leibler, and J. F. Joanny, Macromolecules **20**, 1935 (1987).